Chemical Kinetics: Catalysis

Final Exam: 5/15/01 8-11 am 120 Lattimer

Kinetics Review

From Maxwell-Boltzmann Thru Diffusion to Kinetics
Rate Laws
Determination of Order
Rate equations
Enzymology
Mechanism Diagnosis

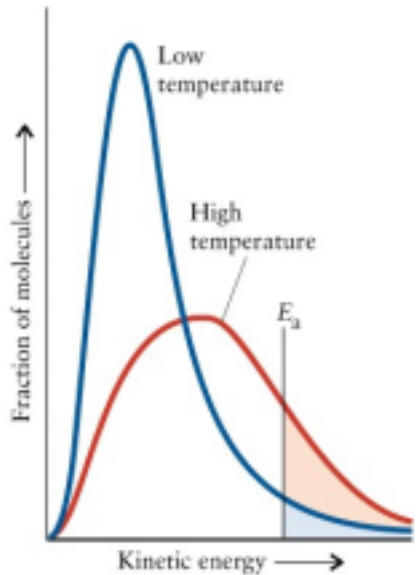
Class Evaluations

Plugging these values back into our original equation for dn_c

$$dn_c = 4\pi N B^3 c^2 e^{-\beta c^2} dc$$

We get:

$$\frac{1}{N}\frac{dn_c}{dc} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}}$$



To calculate the average speed of a molecule:

$$< c >= \int_0^\infty c \frac{1}{N} \frac{dn_c}{dc} dc = \int_0^\infty cP(c)dc$$

Using equations like this is it straightforward to derive:

$$< c >= \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}$$

$$< c^2 >= \frac{3kT}{m}$$

We can now begin to derive some transport properties.

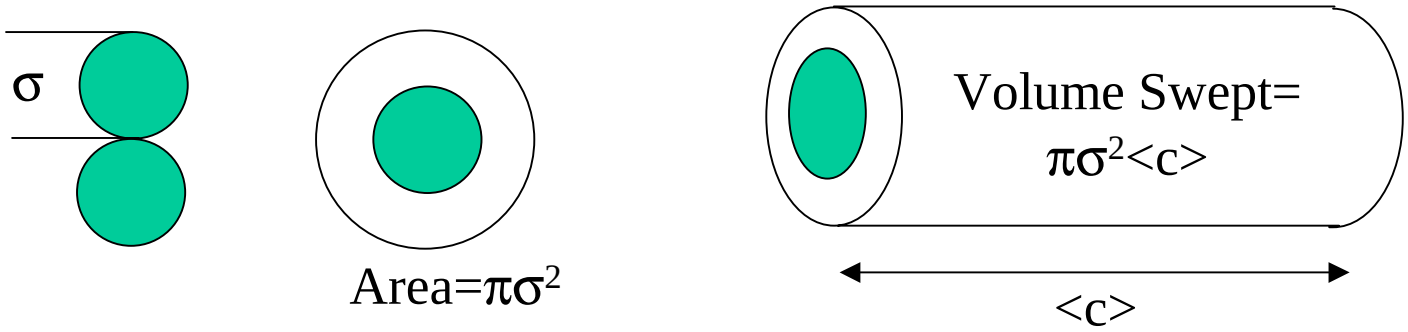
For example the mean free path can be calculated:

λ= mean free path= average distance between collisions

In one second a molecule travels <c>*1s meters and makes Z_1 collisions. Thus:

$$\lambda = \langle c \rangle / Z_1$$

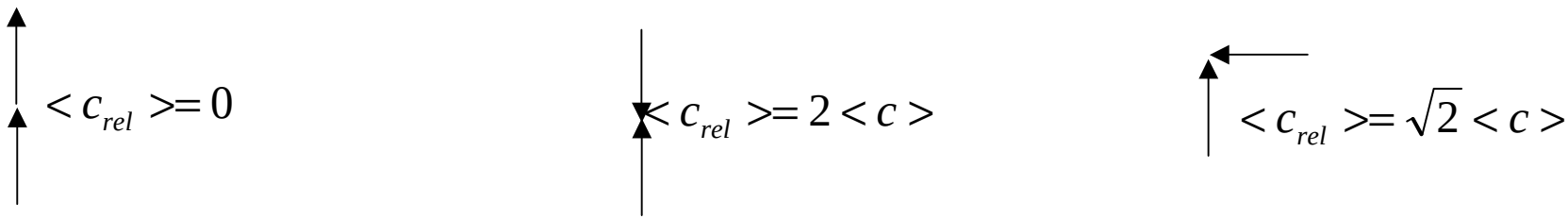
We calculate Z_1 using the following picture



The number of molecules encountered within that volume is:

$$N_1 = \pi\sigma^2 \langle c \rangle * N/V$$

Now the number of collision has comes out of this by realizing that it is the relative velocities that matter!



$$Z_1 = (0.5)^{1/2}\pi\sigma^2 \langle c_{rel} \rangle * N/V$$

$\lambda = \langle c \rangle / Z_1$

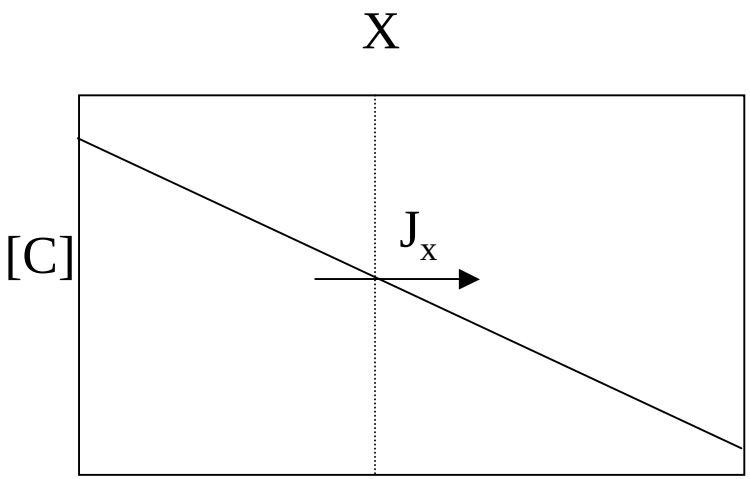
$Z_1 = (0.5)^{1/2} \pi \sigma^2 \langle c_{rel} \rangle * N/V$

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 \frac{N}{V}}$$

Thus the mean free path is dependent on molecular radius and the density of the gas.

At each collision the particle will be deflected off in another direction.

How long does it take a particle to move a given distance from a starting point?

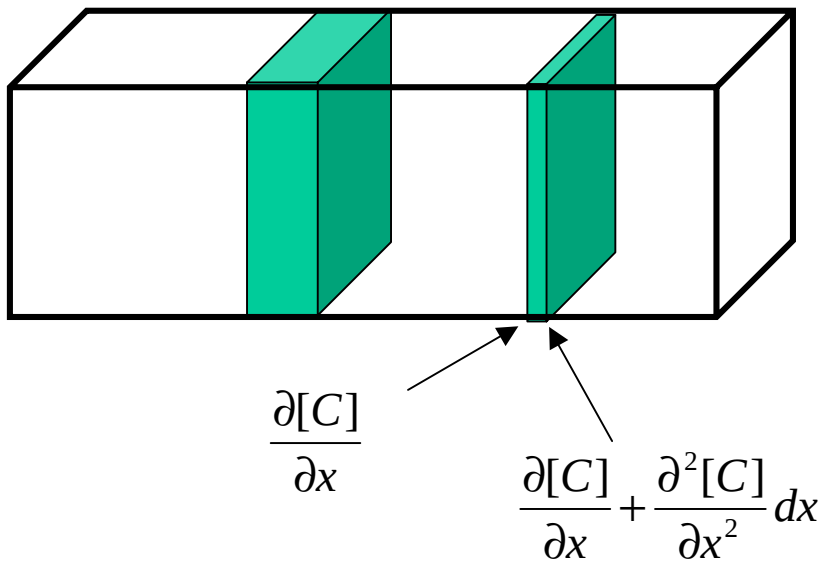


What is found experimentally is that:

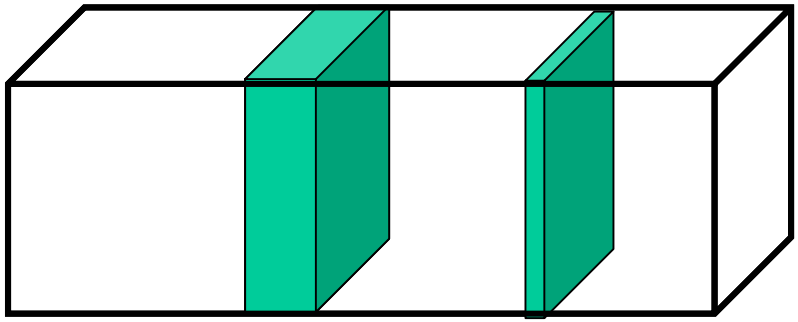
$$J_x \propto A\frac{\partial[C]}{\partial x}$$

$$J_x = -DA\frac{\partial[C]}{\partial x}$$

Fick's First Law



In a small element, the rate of accumulation of material is the flux in minus the flux out.



$\frac{\partial [C]}{\partial x}$ $\frac{\partial [C]}{\partial x} + \frac{\partial^2 [C]}{\partial x^2} dx$

In a small element, the rate of accumulation of material is the flux in minus the flux out.

Rate of entry at x= $J_x = -DA\frac{\partial [C]}{\partial x}$

Rate of entry at x + dx= $J_{x+dx} = -DA\left(\frac{\partial [C]}{\partial x} + \frac{\partial^2 [C]}{\partial x^2} dx\right)$

Rate of Accumulation $= DA\left(\frac{\partial^2 [C]}{\partial x^2} dx\right) = DV_{slice}\frac{\partial^2 [C]}{\partial x^2}$

$$\boxed{\frac{d[C]}{dt} = D\frac{\partial^2 [C]}{\partial x^2}}$$

Fick's second Law

$$\frac{d[C]}{dt} = D\frac{\partial^2[C]}{\partial x^2}$$

Fick's second Law

Fick's second law gives us a relationship between the changing concentration gradient and the time dependence concentration.

Solutions to this equation are well-known!

$$[C] = \frac{const}{t^{1/2}} e^{-x^2/4Dt}$$

Given the original amount of starting material, N, normalization gives us the const.

$$N = \int_{-\infty}^{\infty} c\,dx \quad \Rightarrow \quad const = \frac{N}{2(\pi D)^{1/2}}$$

$$[C] = \frac{N}{2(\pi Dt)^{1/2}} e^{-x^2/4Dt}$$

From this equation it is possible to calculate the amount of material at any volume element, at any position and at any time!

The mean square displacement of a concentration element can simply be calculated from this equation as well!

We know that the amount of a diffusing substance that reached x+dx from x is c*dx. Thus, the mean square displace of this material is:

$$< x^2 >= \frac{1}{N} \int_{-\infty}^{\infty} x^2 c dx = 2Dt$$

So when two molecules react

They have to be within a small enough volume that they can collide

They have to collide with enough energy to overcome the barriers to exchange or rearrangement of material

When we write down equations for kinetics we are assuming average case behavior of a well-stirred (spatially homogeneous) mixture.

$$\lambda = \frac{1}{\sqrt{2}\pi\sigma^2 \frac{N}{V}}$$

The probability for collision depends on density.

The probability of an A,B collision depends on their relative (local?) densities.

And the probability that if they collide they will react depends on the energy of collision.

$$\frac{1}{N}\frac{dn_c}{dc} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} c^2 e^{-\frac{mc^2}{2kT}}$$

So we end up with rates of reaction that, on average, look like:

Rate $\propto$ f(Energy)*g(density A, density B)= k*[A][B]

The rate constant will depend on the kinetic energy, and the barriers (enthalpic and entropic) of forming the transition state.

Rate laws are therefore always polynomial for elementary reactions

$aA + bB \rightarrow cC + dD$ $\qquad v = k*[A]^a[B]^b$

The rate equations for these reactions look like:

$$\frac{dA}{dt} = -v$$

$$\frac{dB}{dt} = -v$$

$$\frac{dC}{dt} = v$$

$$\frac{dD}{dt} = v$$

Solving for equations like these often requires defining a reaction progress.

[A]= A_0-x, [B]=B_o-x

so

$$\frac{dA}{dt} = k[A]^a[B]^b = k(A_0 - x)^a(B_0 - x)^b = \frac{d(A_0 - x)}{dt} = \frac{dx}{dt}$$

Now you can do a separation of variables and solve!

So if you are given a time course for appearance of a given species (say C), then you can examine the production in time and compare it to solutions to different mechanistic hypotheses.

Similarly you can derive half-lives by solving the equations and then solving for the time at which you have exactly half the starting material left.

You only get concentration independent half-lives for first order reactions!

How do you obtain rate constants and orders?

By fitting?

Initial rates!
Reactants in excess!

But remember that rate constants depend on temperature!

And by Arrhenius and Transition State Theory we know how these rates depend on temperature.

By TST we know there we can describe the reaction barriers by thermodynamic constants– thus the same dependencies of these variables on temperature, pressure, non-idealities must exist!

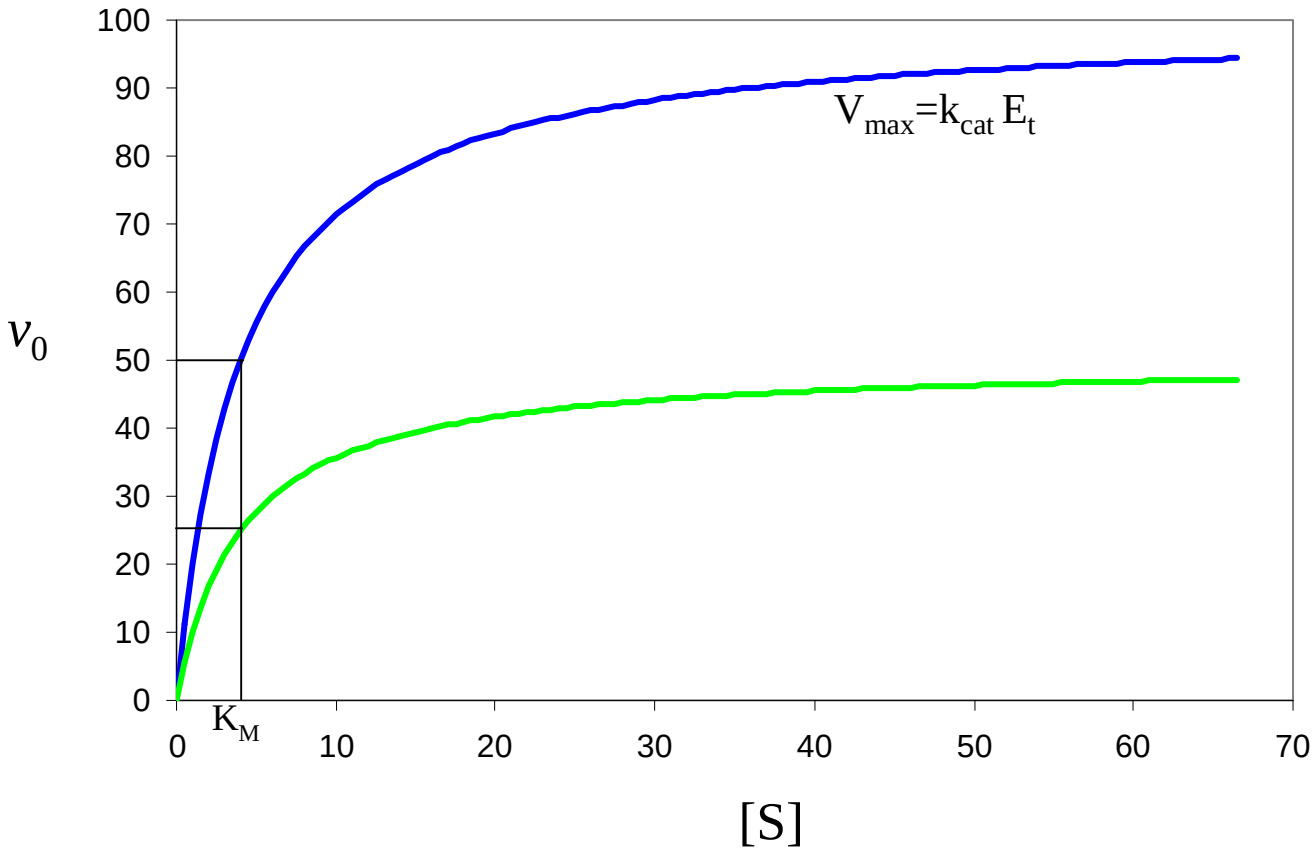
We found for enzymatic reactions a fairly algorithmic way of solving for their rate laws. In all cases this involves:

1) Writing them down as elementary reaction steps
2) Making approximations:
    a) stationary state approximation
    b) rapid equilibrium approximation
    c) conserved total enzyme
    d) large but not too large concentration of S's
    e) small but not too small concentration of E
    f) we are interested in only initial rates

$$
\begin{array}{ccccccccc}
E & + & S & \underset{k_{-1}}{\overset{k_1}{\longleftrightarrow}} & ES & \xrightarrow{k_{cat}} & E & + & P \\
+ & & & & & & & & \\
I & & & & \updownarrow & & & & \\
\updownarrow & & & & & & & & \\
EI & + & S & \longleftrightarrow & EIS & & & &
\end{array}
$$

The rate of product production for a Michaelis-Menten enzyme is thus

$$v_0 = k_{cat}[ES] = k_{cat}\frac{E_t S}{K_M + S}$$



Lineweaver and Burk came up with the following simple transform:

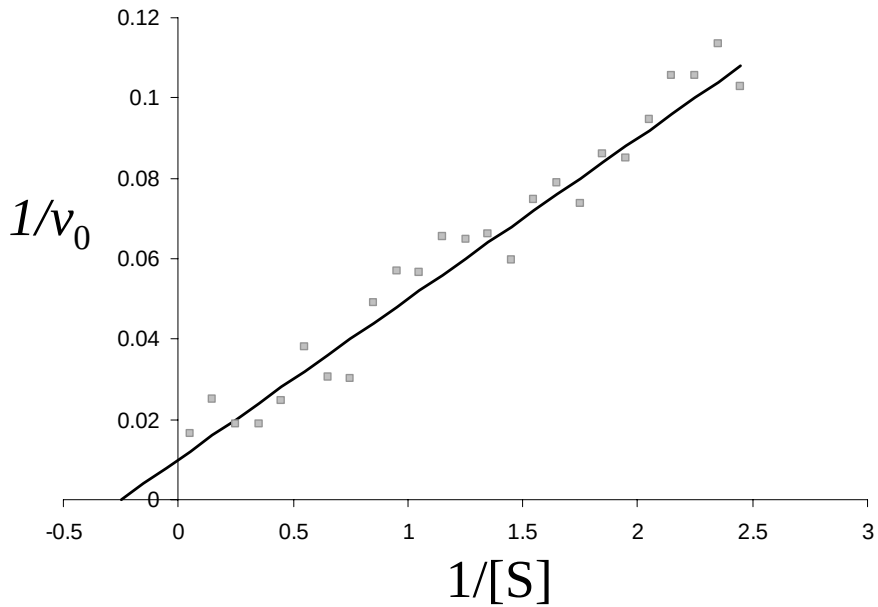
$$v_0 = k_{cat}[ES] = k_{cat}\frac{E_t S}{K_M + S}$$

$$\frac{1}{v_0} = \frac{1}{k_{cat}}\frac{K_M + S}{E_t S} = \frac{1}{V_{\max}}\left(1 + \frac{K_M}{S}\right)$$

So plotting $1/v_0$ versus 1/[S] gives a linear plot with

y-intercept= $1/V_{max}$
slope= K_m/V_{max}

x-intercept= $-1/K_M$



$$[ES] = \frac{E_t[S]}{K_S + [S]}$$

Uninhibited

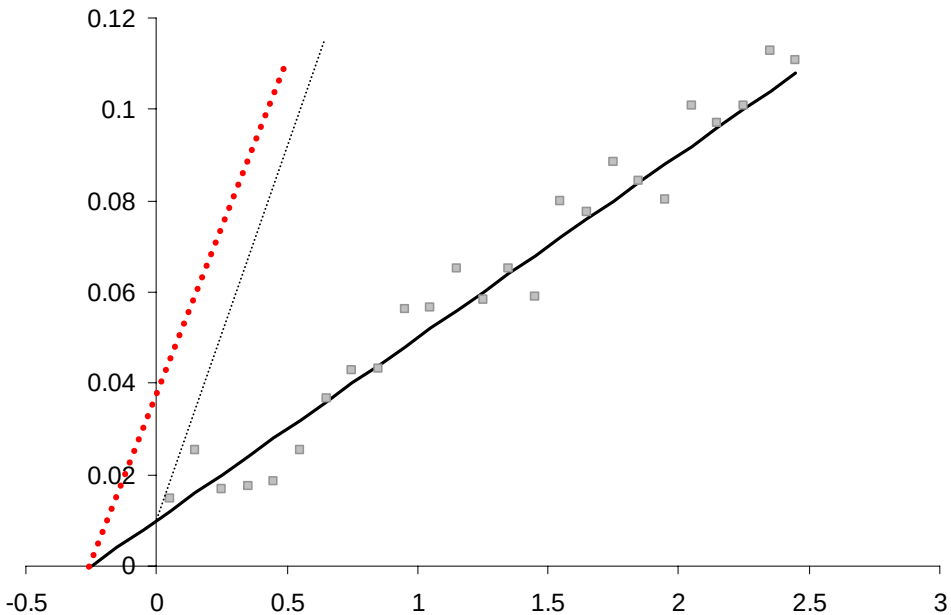
$$[ES] = \frac{E_t[S]}{K_S(1 + \frac{[I]}{K_I}) + [S]}$$

Competitive

$$[ES] = \frac{[S]}{K_S + [S]} \frac{E_t}{\left(1 + \frac{I}{K_I}\right)}$$

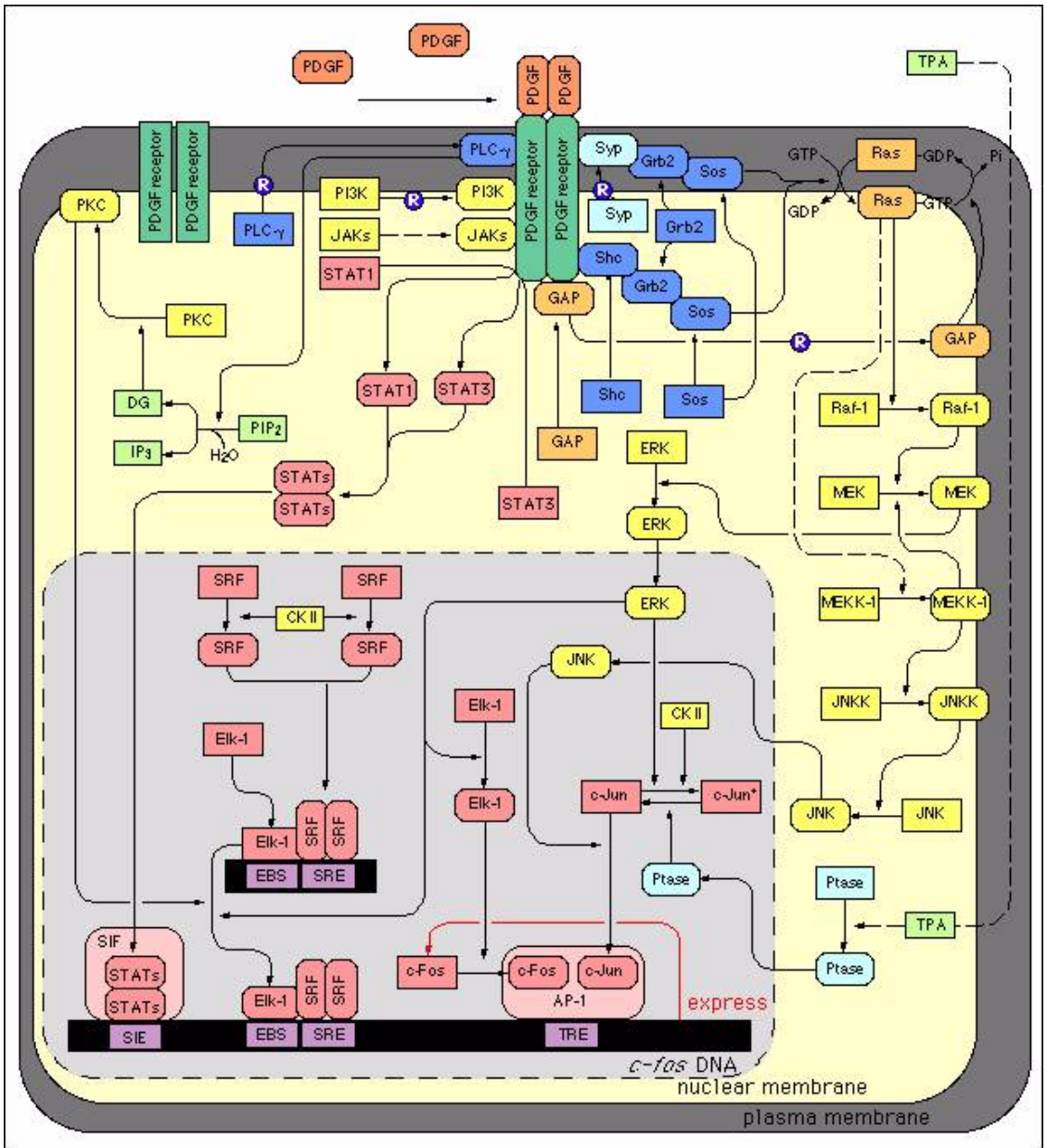
Non-Competitive

What will be the effects on a Linweaver-Burk plot!



y-intercept= $1/V_{max}$
slope= K_m/V_{max}
x-intercept= $-1/K_M$

The spread of cellular function



Thermodynamics
- Spontaneity
- Energy Accounting
- Phase Equilibria
- Electrochemical

Equilibria
- Solubility
- Binding equilibria

Transport
- Diffusion
- Active Transport

Kinetics
- Reaction rates
- Enzymology
- Networks